SUMMARY OF THE INVENTION

This object is achieved by a method for producing a porous carbon article comprising the steps of formation of one or more carbide powders to an intermediate body with transport pores, i.e. pores having a size larger than 100 nm, by shaping, characterised by the further steps of,
selecting the one or more carbide powders on the basis of dependence of specified nanopore size on physical and chemical constants of the carbides using the relationship;

$$X = Z*(1-R)/R$$

where X = specified size of nanopores, nm;

Z = 0.65-0.75 nm;

$$R = \nu M_c \rho_k / M_k \rho_c$$

where M_c - molecular mass of carbon, g/mole;

M_k - molecular mass of carbide, g/mole;

ρ_k - density of carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

ν - number of carbon atoms in carbide molecule,

heat treating the intermediate body in a medium of gaseous hydrocarbon or hydrocarbon mixtures at a temperature exceeding the decomposition temperature for the hydrocarbon or hydrocarbons until the mass of the intermediate body has increased at least 3% thereby creating a workpiece in the form of a rigid carbonaceous skeleton,
thereafter thermochemically treating the work piece in a medium of gaseous halogens
to provide predetermined nanopore sizes, i.e the pores have a size less than 10 nm, a predetermined volume of nanopores, and a predetermined distribution of nanopores within the volume of the article, the carbides used forming carbons

having a slot-like structure. By this method materials having controlled and predetermined nanopores, an optimal ratio between volumes of transport pores and nanopores, high mechanical strength and complicated shapes can be produced.

In a preferred embodiment elements from III, IV, V or VI group of Mendeleyv's Periodic system are selected as carbon precursor.

The formulation of carbide particle mixture is chosen in dependence of desired distribution of nanopores by sizes using the relationship;

$$\Psi_i = K_i\varphi_i / \sum K_i\varphi_i$$

where Ψ_i - volumetric part of nanopores with size x_i in total volume of nanopores;

φ_i - volumetric part of i-th carbide in particle mixture;

n - number of carbides;

$$K_i = 1 - \nu M_c\rho_{ki} / M_{ki}\rho_c$$

where M_c - molecular mass of carbon, g/mole;

M_{ki} - molecular mass of it-h carbide, g/mole;

ρ_{ki} - density of it-h carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

ν - number of carbon atoms in carbide molecule.

The intermediate body is formed with a porosity of 30-70 vol%, preferably 35-50 vol%, the porosity being determined with the following relationship;

AMENDED SHEET

5 amended

$$\varepsilon_0 = [1 - \nu_{np} / \Sigma K_i \varphi_i] * 100$$

where ε_0 - porosity of intermediate body, vol%;

φ_i - volumetric part of i-th carbide in particle mixture;

ν_{np} - predetermined volumetric part of nanopores in final article;

$$K_i = 1 - \nu M_c \rho_{ki} / M_{ki} \rho_c$$

where M_c - molecular mass of carbon, g/mole;

M_{ki} - molecular mass of it-h carbide, g/mole;

ρ_{ki} - density of it-h carbide, g/ccm;

ρ_c - density of carbon, g/ccm;

ν - number of carbon atoms in carbide molecule.

The treatment in a medium of gaseous hydrocarbon or hydrocarbon is carried out until the mass of the intermediate body has changed according to the following relationship;

$$\Delta m = Q(\varepsilon_0 - \nu_{tr}) / (1 - \varepsilon_0)$$

where Δm - relative change of intermediate body mass, g/g;

ε_0 - porosity of intermediate body, vol%;

ν_{tr} - predetermined volumetric content of transport pores, vol%;

$$Q = \rho_c / \rho_{mix}$$

Where ρ_c = density of carbon, g/ccm;

AMENDED SHEET

6 amended

ρ_{mix} = density of carbides mixture, g/ccm;

The intermediate body can be formed by pressing. Other well known forming methodes, such as slip casting, tape casting or slurry casting and injection moulding can of course also be used. nNatural gas is used as a mixture of hydrocarbons and the treating in hydrocarbon medium is carried out at 750-950° C.

Alternatively at least one of the hydrocarbons used during the treatment of the intermediate body in hydrocarbons medium is selected from the group of acetylene, methane, ethane, propane, pentane, hexane, benzene and their derivatives and the treating in hydrocarbon medium is carried out at 550-1200 °C.

The particles of carbide or carbides of which the intermediate body is formed are arranged uniformly or nonuniformly throughout its volume.

The thermochemical treatment of the workpiece is carried out in a medium of gaseous halogens at 350-1200°C, preferably chlorine. at 500-1100°C.

The present invention relates also to a porous carbon article having nanopores, i.e pores having a size less than 10 nm, and transport pores, i.e. pores having a size grater than 100 nm, characterised in that the article consists of a rigid carbon skeleton in which at least 3 % of its mass consists of carbon without nanopores.

In an embodiment the article has nanopores of at least two sizes. Furthermore, the volume of nanopores is 15-50 % and the volume of transport pores is 10-55 % the nanopores are

AMENDED SHEET

distributed uniformly or nonuniformly throughout the volume of the article.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will now be described with reference to the following figures, of which;

Fig.1 shows a table of the properties of materials produced in example 1, and

Figs. 2 disclose porosimetry data for the sample of example 1 .

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

The method according to the invention comprises the following steps:

1) Forming a workpiece with transport porosity using particles of a carbide or carbides of elements from III, IV, V and VI groups of Mendeleyev's Periodic System, in the form of a rigid carbonaceous skeleton containing in its structure particles of a carbide or carbides selected from the said groups and arranged in a predetermined order providing formation in the subsequent steps desired transport porosity and nanoporosity by sizes, volume and distribution of pores throughout the volume of the article;

2) Formation of nanoporosity throughout the volume of a workpiece obtained in the 1st step by thermochemical treatment of the said workpiece in gaseous halogens, such as chlorine, at elevated temperatures in the range of 350 to 1200°C, preferably 500-1100°C.

Current notions of carbon materials structure point out that nanopores generated during the thermochemical treatment process are formed by ordered or disordered graphite planes of carbon, which for simplicity might be considered as shaped as slots, the width of the latter depending on type of carbide used for forming of the workpiece with transport porosity.

These theoretical ideas are in good agreement with experimental data which allowed the inventors to disclose the following dependence for carbon materials having such structure:

amended

Under these conditions a decomposition of hydrocarbon occurs by reaction;

$$C_mH_n \rightarrow mC + {}^{n}/_{2}H_2\uparrow \qquad (2)$$

with deposition of the generated pyrocarbon on the surface and in the pores of intermediate body volume.

The specified range of initial porosity is based on the fact that at a porosity below 30% it is difficult to obtain sufficient volume of transport pores in the article providing access of adsorptive to nanopores where adsorption process occurs and at a porosity above 70% the article does not possess satisfactory mechanical strength.

The value of 35-50 vol% is preferable because it is easily achieved by any available method of workpiece forming and it assures an optimal relation between volumes of transport pores and nanopores in the article.

The size and distribution of the transport pores can be controlled by selecting appropriate particle sizes and particle distribution. The amount of possible particle packing due to the forming process will of course also influence the porosity of the work piece.

Calculation of concrete value of intermediate body porosity necessary to obtain a predetermined volume of nanopores, is carried out using the following expression:

$$\varepsilon_0 = [\, 1 - v_{np} / \sum_{i=1}^{n} K_i \varphi_i \,] \cdot 100 \qquad (3)$$

where ε_0 - porosity of intermediate body, vol%;

φ_i - volumetric part of i-th carbide in powder mixture;

AMENDED SHEET

The needed mass change of the intermediate body during pyrocarbon deposition is calculated by formula (4), assuming a transport porosity of 35 vol%

Then, $\Delta m = [0.4476(46-35)/(100 - 46] \cdot 100 = 9.1\%$

A mixture is prepared using 5.01 g of TiC powder with a size of the particles of 20 μm. Ethyl alcohol is added in the amount of 10% of the mass of the mixture. Then, an intermediate body is formed by pressing on a hydrostatic press machine (P-125) at 30 ± 1 Mpa pressure. After the pressing, the intermediate body is dried at 150 ± 10°C during 1-1.5 hour until complete removal of temporary binder.

This is followed by pyrocarbon deposition on the intermediate body b means of heat treatment in natural gas medium at atmospheric pressure in a quartz continuous reactor at 850°C during 12 hours until change of mass by 9.1%.

Then, the sample is chlorinated. The chlorination is carried out in a isothermal quartz reactor at 650°C during 4 hours. Then a blow-through of the reactor with argon at a temperature of 800°C is carried out to remove excessive chlorine out of the reactor zone and the internal surface of the sample.

Properties of the obtained material are presented in Table 1. From this table it is evident that the measured peak value of the nanopore size measured by gas porosimetry correspond to the calculated value.

Two articles produced according to Example 1 were saturated with 20% KOH solution by boiling and placing them in an electrolyte solution (20% KOH). Opposite by sign potential was applied to each of the articles to form a double electric layer in the material nanopore volume. In this case the spe-

16 amended

cific electrical capacitance of the double electric layer formed in the material was 37.8 F/g.

Notes:

1) Total volume of pores is determined by hydrostatic method according to GOST 473.4-81.
2) Nanopore volume is determined by exsiccator method by adsorption of benzene under static conditions, see "Fundamentals of adsorption technology." Keltsev N.V., Moscow, Chemistry publishers, 1984, p. 33.
3) Transport pore volume is determined by formula

$$V_{tr} = V_{\Sigma} - V_{np}.$$

4) Size of nanopores is determined by means of mercery and gas porosimetry (Micromeretics Auto Pore III and Micromeretics ASAP 2010, respectively). Data are shown in Figures 2-4. Legend Hg denotes mercury porosimetry intrusion data, legend BJH denotes gas porosimetry desorption data analysed by the BJH method, and legend Micro denotes gas porosimetry data analysed by the Horvath-Kawazoe method.

The presented data allows one to draw the conclusion that a new method for producing a porous carbon article comprising transport pores and nanopores with controllable sizes and distribution of nanopores throughout its volume as well as

AMENDED SHEET